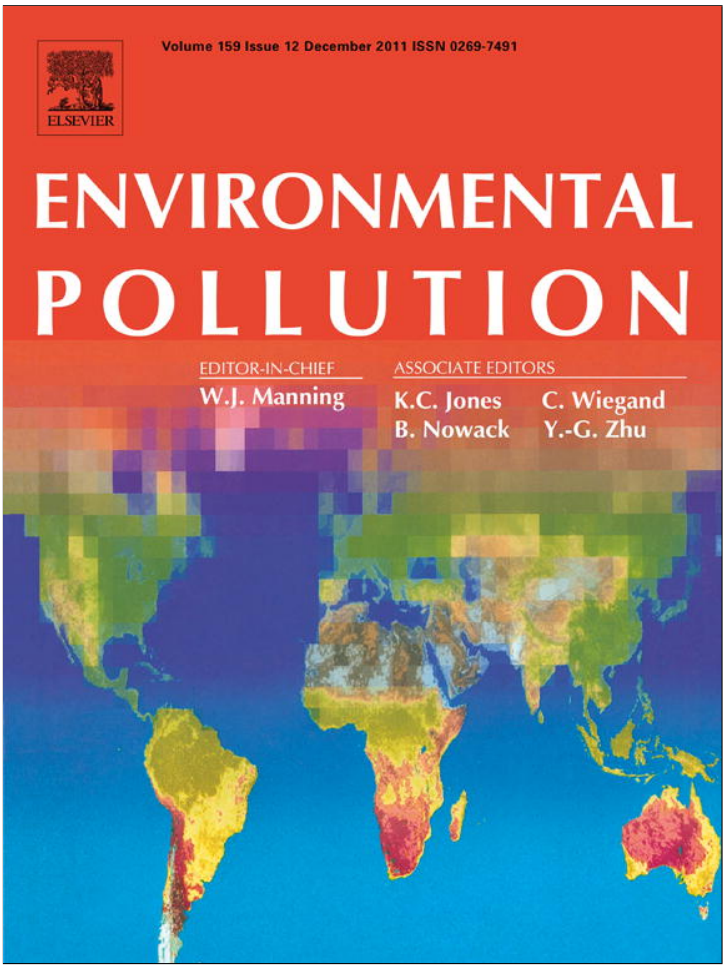

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Polychlorinated naphthalenes (PCNs) in riverine and marine sediments of the Laizhou Bay area, North China

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ABSTRACT

PCN congeners were analyzed in marine and riverine sediments of the Laizhou Bay area, North China. Concentrations of PCNs ranged from 0.12 to 5.1 ng g^{-1} dry weight (dw) with a mean value of 1.1 ng g^{-1} dw. The levels of PCNs varied largely, with industrial group approximately ten folds higher than those of the rural in riverine sediment. A strong impact by direct discharge from local factories was suggested. Similar compositional profiles were found within groups. High resemblance of compositional profiles between industrial samples and Halowax 1014 was observed. It was indicated that PCNs in riverine sediments were mainly from release of industrial usage, with additional contributions from industrial thermal process at certain sites. In marine sediments, it was suggested that PCNs along the coast of Laizhou Bay were mainly controlled by riverine input. While in the central bay, PCN distributions were possibly impacted by combined multiple factors.

1. Introduction

Polychlorinated naphthalenes (PCNs) are a group of environmental contaminants comprised of 75 congeners based on the number and position of chlorine in naphthalene ring system. They were previously widely used in industrial applications, such as cable insulation, wood preservation, engine oil additives, electroplating masking compounds, dye carriers, capacitors and refracting index testing oils in 20th (Falandysz, 1998). Commercial products include Basileum, N-oil, N-wax, Perna wax, Nibren waxes, Halowax, Seekay waxes, Woskol, Cerifal materials, Clonacire waxes and other technical CN formulations (Falandysz, 1998; Falandysz et al., 2008, 2000, 2006; Yamashita et al., 2003). Some of the PCN congeners exhibit dioxin-like effects to mammalian animals (Sisman and Geyikoglu, 2008; Villeneuve et al., 2001; Vinitskaya et al., 2005). Due to their accumulation in organisms, the toxicity could be enhanced. PCNs can be released into the environment from various pathways. Although the production and usage of technical PCN formulations has declined since early 1980s, products containing these formulations are still present in the environment (Kannan et al., 1998). In addition to the release from historical usage of technical formulations, PCNs are also leaked out from impurities of technical PCB preparations and from unlawfully usage in recent years (Falandysz, 1998; Yamashita et al., 2000a). Despite of the phasing out of technical CN formulations, PCNs were detected in sites near chemical industries, such as Chlor-Alkali plants, petrochemical industries, metal refineries, municipal waste incineration plant, and etc (Ba et al., 2010; Brack et al., 2003; Castells et al., 2008; Helm and Bidleman, 2003; Jansson et al., 2008; Kannan et al., 1998; Liu et al., 2010; Llobet et al., 2007). Researches have also shown that PCNs can be unintentionally formed and released through thermal processes such as municipal waste incineration and nonferrous metallurgy process (Jansson et al., 2008; Oh et al., 2007). A latest study reported that secondary nonferrous metallurgical facilities in China are a bigger contributor than waste combustion of PCNs at present (Ba et al., 2010).

Information on production of technical PCN formulations in China was not available. A few reports have revealed that PCN levels in sediments of China are comparable to some regions in developed countries (Pan et al., 2007). A recent Global Atmospheric Passive Sampling (GPAS) study has shown PCN levels in the air of Chinese cities were relatively high globally and reemission of industrial PCN was indicated (Lee et al., 2007). However, there's very few data of PCNs in China, especially in the coastal region, where large cities and industrial parks concentrated.

Laizhou Bay is one of the three main bays of Bohai Sea, making up 10% of the total area (Wang et al., 2007). It is a shallow bay with smooth submarine topography and a submerged gentle slope from coast to the open sea. Its average water depth is less than 10 m with maximum of 18 m. Due to the large volume of freshwater input

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from the Yellow River, tidal current in the bay is very complicated. Besides, Laizhou Bay is one of the most easily affected bays by storm tide in China. Due to its coastal morphology and the location on the intersection of warm and cold air masses, Laizhou Bay could be threatened by storm tide all the year round (Peng et al., 2010).

Around the bay, industrial and urban developments have been booming in the last decades. The famous chemical industrial base – Weifang Binhai Economic Development zone (shorten as Binhai Zone), is located to a large extent along the coast, due to the abundant seawater resources and underground brine resources. Over 400 chemical enterprises are located nearby and more than 150 chemical products were manufactured in this area. Among them, chlor-alkali industry is one of the major industries in this Zone, which has a long history of development since 1930s and has developed rapidly in recent twenty years. Now it has become the biggest manufacturing base of some chlor-alkali products, such as calcined soda, calcium chloride, polyvinyl alcohol water glass and saleratus, in Asia or even in the world. On the northwest coast, there is the second largest oilfield (Shengli oilfield) of China and thus petrochemical industries are well developed due to the abundant oil resources. Huge amounts of domestic sewage and industrial wastewaters are discharged into Laizhou Bay directly.

This study intends to investigate the distribution and levels of PCNs around Laizhou Bay area via a large survey of surface sediments in the river systems, each representative of different levels of anthropogenic activities, as well as in marine sediments of Laizhou Bay. Given the encouraged growth of chemical industries and marine fishery in Laizhou Bay, Information about PCN contamination status and its effect on marine biota was urgently needed.

2. Materials and methods

2.1. Study area and sample collection

The study area and sampling sites are shown in Fig. 1. There are twelve tributaries in different sizes which flow into Laizhou Bay, including the Yellow River (also named as Huanghe River, HH), Yihong River (YHH), Guangli River (GLH), Zimaigou River (ZMG), Xiaoqing River (XQH), Mihe River (MH), Bailang River (BLH), Dihe River (DH), Yuhe River (YH), Weihe River (WH), Jiaolai River (JLH) and Dajiawa drainage system (DJW). HH is the biggest river with the largest river runoff and landslide discharge, followed by XQH, WH and JLH.

River sediments are here classified into three categories according to their surrounding environment that predominantly impacts them: (1) industrial; (2) urban; (3) rural. In the industrial group, DH1 and DH2 were sampled in an area scattered with dyeing, printing, textile and sugar industries in addition to chemical plants. Other industrial sites were influenced mostly by chemical or petrochemical industries. The estuarine sediments are not included into any group. Besides, site WFG was located within Weifang port, which was undergoing sea reclamation with large amounts of fresh soil transported and mixed into sediments. Thus the sediments were probably strongly influenced by complex process while being sampled and cannot reflect the true sedimentary information. It is not included into any group.

All samples were collected between September 14 and October 17, 2009, using a stainless steel grab sampler. They are thirty-two surface sediments (top 0–10 cm) from ten river and drainage system sites, four river estuary sites and twenty-six marine sites. All the samples were transported on ice to laboratory and then stored at −20 °C until analyzed.

2.2. Extract and cleanup

Freeze-dried sediment samples (20 g dry weight) were homogenized and Soxhlet extracted in dichloromethane (DCM) for 24 h, with 2,4,5,6-tetrachloro-*m*-xylene (TC*m*X) and PCB 209 added prior to extraction as recovery surrogates. The extract was reduced to 1 mL by rotary evaporation and then transferred to a glass column (15 cm long, 0.7 cm i.d.) filled with 1 cm anhydrous sodium sulphate and 3 cm acidified silica gel/sulphuric acid (50% w/w concentrated sulphuric acid). It was eluted with 15 mL hexane (HEX) and concentrated to 0.5 mL under a gentle N_2 for cleanup on silica columns, which packed with 3 cm pre-rinsed silica gel (3% deactivated) and 1 cm anhydrous Na_2SO_4 on the top. Fractionation was achieved with the solvent sequences of 15 mL of HEX (F1) and 15 mL DCM/HEX (1:1 in volume, F2). Fraction F1 contained all the PCNs and was reduced to 25 uL under a gentle stream of N_2. 20 ng of quintozene (PCNB) was added as internal standards before instrumental analysis.

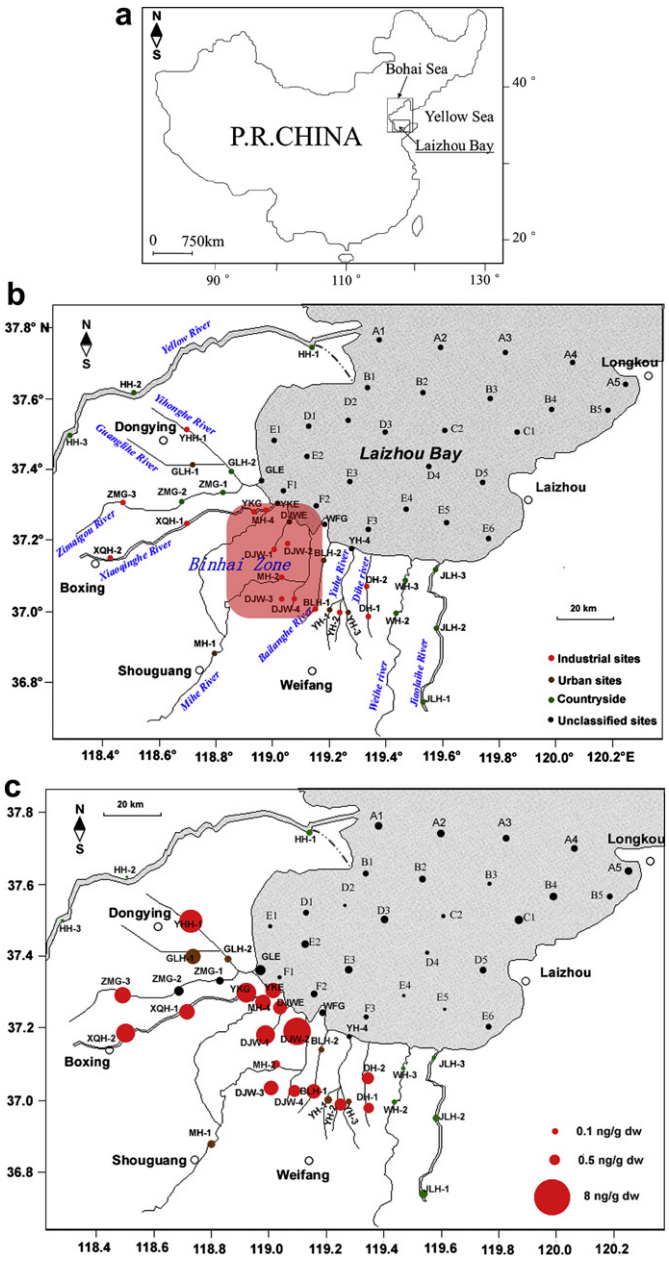

Fig. 1. (a) Location of Laizhou Bay in China; (b) Map of riverine and marine sampling sites (c) Geographic distributions of PCN concentrations in riverine and marine sediments of Laizhou Bay.

2.3. Instrumental analysis

PCNs were analyzed by gas chromatography–electron-capture negative-ion mass spectrometry (GC–ECNI-MS) using a HP 7890 GC-5975 MSD in selected ion monitoring mode on a DB-5ms column (30 m × 0.25 mm i.d. × 0.25 um film thickness, J&W Scientific) and methane as the reagent gas. The temperature program was 80 °C for 0.50 min, 15 °C/min to 160 °C, 3 °C/min to 265 °C and held for 5 min. The inlet, transfer line, ion source, and quadrupole temperatures were 265 °C, 280 °C, 150 °C, and 150 °C, respectively. The target/quantifier ions were 232/230 for tri-, 266/264 for tetra-, 300/298 for penta-, 334/332 for hexa-, and 368/366 for hepta-, and 404/402 for octachloronaphthalene (Carrizo and Grimalt, 2006). Tri- to octa-CNs were quantified against a Halowax1014 technical PCN mixture (∑PCNs = Tri-Cl: PCN-19, -21, -24, -14, -15, -16, and -23; Tetra-Cl: PCN-42, -33/34/37, -47, -36/45, -28/43, -27/30/39, -32, -35, -38/40, and -46; Penta-Cl: PCN-52/60, -58, -61, -50, -51, -54, -57, -62, -53, -59, and -49; Hexa-Cl: PCN-66/67, -64/68, -69, -71/72, -63, and -65; Hepta-Cl: PCN-73, and -74; and Octa-Cl: PCN-75). Peaks were quantified only if the signal/noise ≥ 4. The limit of detection (LOD), defined as a signal of 4 times the noise level, ranged from 0.02 to 0.07 ng g^{-1} for all the peaks including those coeluted compounds.

Sediment total organic carbon (TOC) was determined with an elemental analyzer (CHNS Vario Ei III, Elementar) after removal of carbonates with hydrochloric acid.

2.4. QA/QC

For each batch of 20 field samples, a procedural blank (solvent with a filter paper identical to that used to wrap the sediment) and a sample duplicate were processed. Only a few congeners with very low concentrations were found in procedural blanks and they were appropriately subtracted from those in the sample extracts. Three duplicate samples reported RSDs within 20% for all the target chemicals. The recoveries for TC*m*X and PCB 209 were 87.1 ± 12.5% and 85.8 ± 9.8%, respectively. All reported values were not corrected by surrogate recovery.

3. Results and discussion

3.1. PCN concentrations and geographical distribution

PCN distributions are shown in Fig. 1c. The concentrations of PCNs ranged from 0.06 to 0.47 ng g^{-1} dw and from 0.05 to 5.1 ng g^{-1} dw with a mean value of 0.26 ng g^{-1} dw and 1.1 ng g^{-1} dw for marine sediments and river sediments, respectively. According to the classification of river samples described in Section 2.1, distinct concentration gradient was observed among the three groups. On an average level, ∑PCNs decreased in the order: industrial area (2.0 ng g^{-1} dw) > urban area (0.44 ng g^{-1} dw) > rural (0.20 ng g^{-1} dw). It was approximately ten times higher in industrial area than in rural area. The highest concentration was found at site DJW2 (5.1 ng g^{-1} dw), followed by YHH1 (3.6 ng g^{-1} dw), YKG (2.7 ng g^{-1} dw), XQH2 (2.5 ng g^{-1} dw) and DJW1 (2.4 ng g^{-1} dw). It is reasonable as they are all collected in industrial area. Concentrations of the other samples were below 2.0 ng g^{-1} dw. As for individual rivers, some exhibited a decrease trend from the upper reaches to the lower reaches, like ZMG, JLH and BLH, and some were opposite such as MH. In Xiaoqinghe River, site XQH2, located in the middle relative to the other sites in this river, the concentration is lower than both of the latter two sites. Thus a strong impact by direct discharge from local factories was suggested. This is further proved by the poor correlation between PCN concentrations and TOC in riverine sediments ($r^2 = 0.13$).

According to the samples' surroundings, DJW2 and DJW1 are right located downstream the effluent of a wastewater treating plant and a sewage ditch of two separate marine chemical plants. XQH2 is located nearby a petrochemical plant, while YHH1 was sampled on Shengli Oil Field. YKG is located in Yangkou Harbour, where many cargo ships moored, loaded and unloaded raw chemical materials and products. Thus the PCN contamination might be contributed from multiple industrial activities. Eight samples collected in the suburbs from the Yellow River, Jiaolai River and Weihe River have the lowest PCN levels with concentrations lower than 0.2 ng g^{-1} dw. This is probably attributable to the fact that these rivers flow through a vast farmland and also to the sandy characteristics of these samples.

There are little reports about PCNs in China. Pan et al. investigated PCN concentrations in sediments collected from Qingdao coast sites with a concentration of 0.2–1.2 ng g^{-1} dw, similar with the PCN levels in marine sediments of Laizhou Bay found in our study (Pan et al., 2007). Compared to PCN levels in sediments found in other regions (Table 1), such as backgrounds in Sweden (0.14–7.6 ng g^{-1} dw) (Jaernberg et al., 1993), Venice lagoon (0.03–1.51 ng g^{-1} dw) (Eljarrat et al., 1999), Gdansk basin of Batic Sea (6.7 ng g^{-1} dw) (Falandysz et al., 1996), Gulf of Bothnia (0.27–2.8 ng g^{-1} dw) (Lundgren et al., 2003), coast of Barcelona (0.17–3.27 ng g^{-1} dw) (Castells et al., 2008), lake Ontario (21–38 ng g^{-1} dw) (Helm et al., 2008), Tokyo bay (1.81 ng g^{-1} dw) (Yamashita et al., 2000b), PCN levels in marine sediment of Laizhou Bay were at the lowest end of the range, while the levels in the rivers were similar with many studies in Europe, including the background sites, bays and coastal sites.

Table 1
PCN concentrations in sediments found in other regions of the world.

Locations	Concentrations (ng g^{-1} dw)	References
Sweden	0.14–7.6	Jaernberg et al., 1993
Venice lagoon	0.03–1.51	Eljarrat et al., 1999
Batic Sea	6.7	Falandysz et al., 1996
Gulf of Bothnia	0.27–2.8	Lundgren et al., 2003
Barcelona coast	0.17–3.27	Castells et al., 2008
Qingdao coast	0.2–1.2	Pan et al., 2007
Lake Ontario	21–38	Helm et al., 2008
Tokyo bay	1.81	Yamashita et al., 2000b
Bitterfeld, industrial area	2540	Brack et al., 2003
Georgia coast, former industrial area	23 400	Kannan et al., 1998

3.2. Compositional profiles in riverine sediments

Quite similar compositional profiles of PCNs were observed within sample groups, while it differs among the groups (Fig. 2a). Urban group shows a very high proportion of hexa-CNs (63 ± 13%). While in the rural group, fewer hexa-CN congeners were detected. They have a higher proportion of lower molecular PCNs with the sum of tri-CNs, tetra-CNs and penta-CNs accounting for more than 70% of the mass. Industrial group (exclude DH1 and DH2) was dominant by penta- and hexa-CN homologues. It was 45 ± 9% and 32 ± 4% for penta- and hexa-CNs, respectively. Fig. 2b shows that the increase of PCN concentrations from the rural to urban and industrial areas, and this was mainly contributed by penta-CNs, followed by hexa-CNs. At DJW2, YHH1 and XQH2, tri- and tetra-CNs were relatively higher than other industrial sites, while the levels of penta- and hexa-CNs were similar among the industrial sites. At DH1 and DH2, samples were collected in a different industrial area mentioned in Section 2.1. Compared to other chemical industrial samples, these two samples have a higher abundance of tetra- and hepta-CN congeners and distinct lower proportion of penta-CNs.

Congener patterns were also quite similar within sample groups. Profiles of penta- and hexa-CN homologues were almost identical between industrial sites. Fig. 3 compares congener patterns of some typical industrial samples to Halowax 1014. Despite a more or less batch-to-batch variations of homologue patterns and isomer content were found in recent studies for Halowax 1014, we used the well investigated one in literatures for comparison (Falandysz et al., 2006). High resemblance of penta- and hexa-CN congener patterns was observed. In urban areas, although much less congeners were detected, similarity in hexa-CNs still can be observed. At DH1 and DH2, in spite of the differences in homologue profiles with other industrial samples, patterns of hexa-CNs were also in agreement with Halowax 1014. Thus it can be suggested that hexa-CN congeners in riverine sediments of the Laizhou Bay area were probably mainly from release of similar industrial usage or chemical materials. While the different homologue profiles between Dihe River (DH1 and DH2) and other industrial sites were possibly attributable to their textile and printing industries near these two sites instead of chemical industries in other sites.

3.3. Correlations among PCN homologues and sources identification

In order to further investigate PCN sources in the Laizhou Bay area, correlations between PCN homologues were calculated. Good

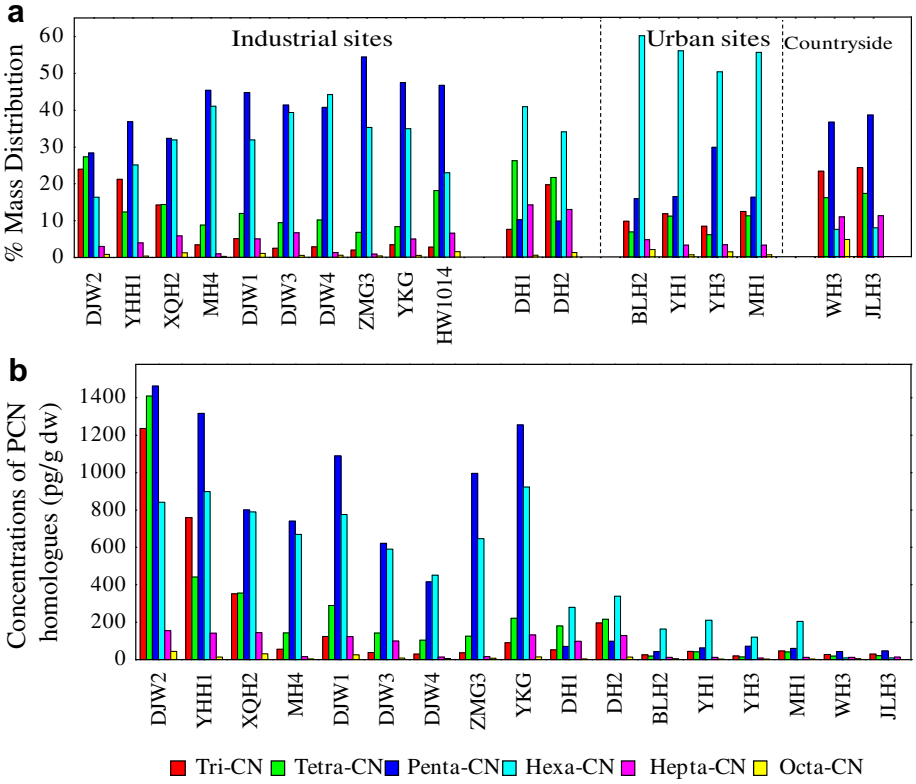

Fig. 2. (a) Mass percent of PCN homologue distributions in river sediments (b) Concentrations of PCN congener groups in river sediments.

correlations were found between penta-CNs and hexa-CNs, tri-CNs and tetra-CNs (Fig. 4a, b), while correlations between lower chlorinated naphthalenes (sum of tri-CNs and tetra-CNs) and higher molecular weight (sum of penta-CNs, and hexa-CNs) were not that good (Fig. 4c). However, after a few sites were removed, their correlations were greatly improved (Fig. 4d). It can be indicated that industrial usage was also the main source of lower chlorinated congeners in most sites. The few removed sites mainly include DJW2, YHH1 and XQH2. They have remarkably higher percent of tri- and tetra- homologues, while penta- and hexa-CN congeners were at the similar level (Fig. 2) with other industrial samples. According to samples' surroundings, these sites were obviously impacted by industrial thermal process, such as thermoelectricity and oil refining in addition to chemical industries. Many studies have shown that lower chlorinated congeners were prone to be formed during combustion or incineration process, while in technical PCN and PCB formulations, most products were dominant by highly chlorinated congeners (Helm and Bidleman, 2003; Liu et al., 2010; Wang et al., 2006; Yamashita et al., 2000a). Considering the high resemblance of profiles between industrial samples and

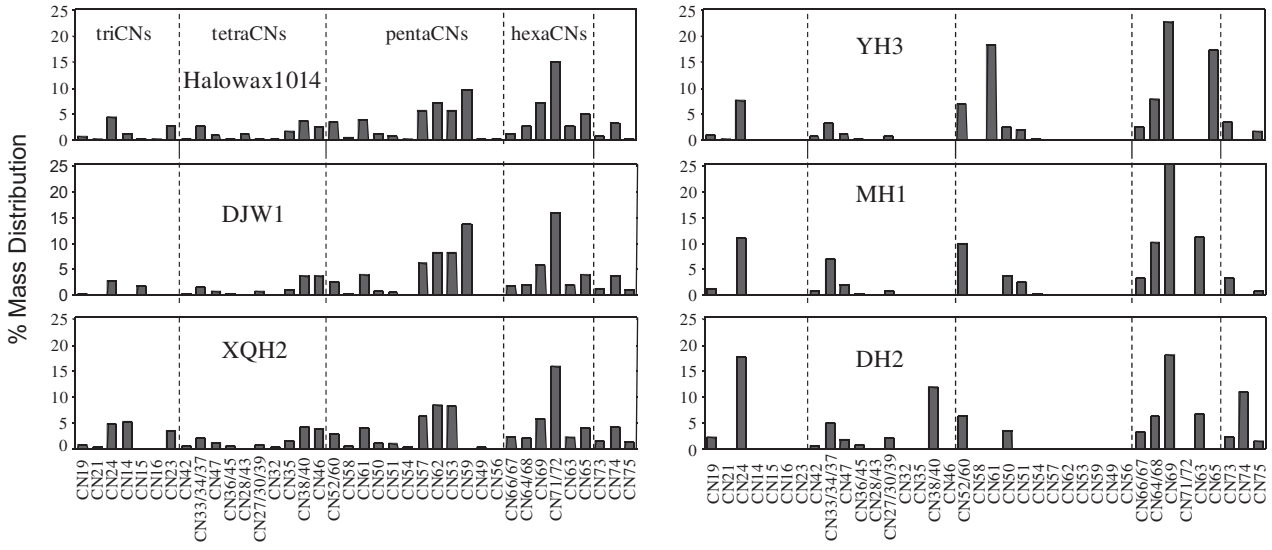

Fig. 3. Congener patterns of PCNs in river sediments and Halowax 1014.

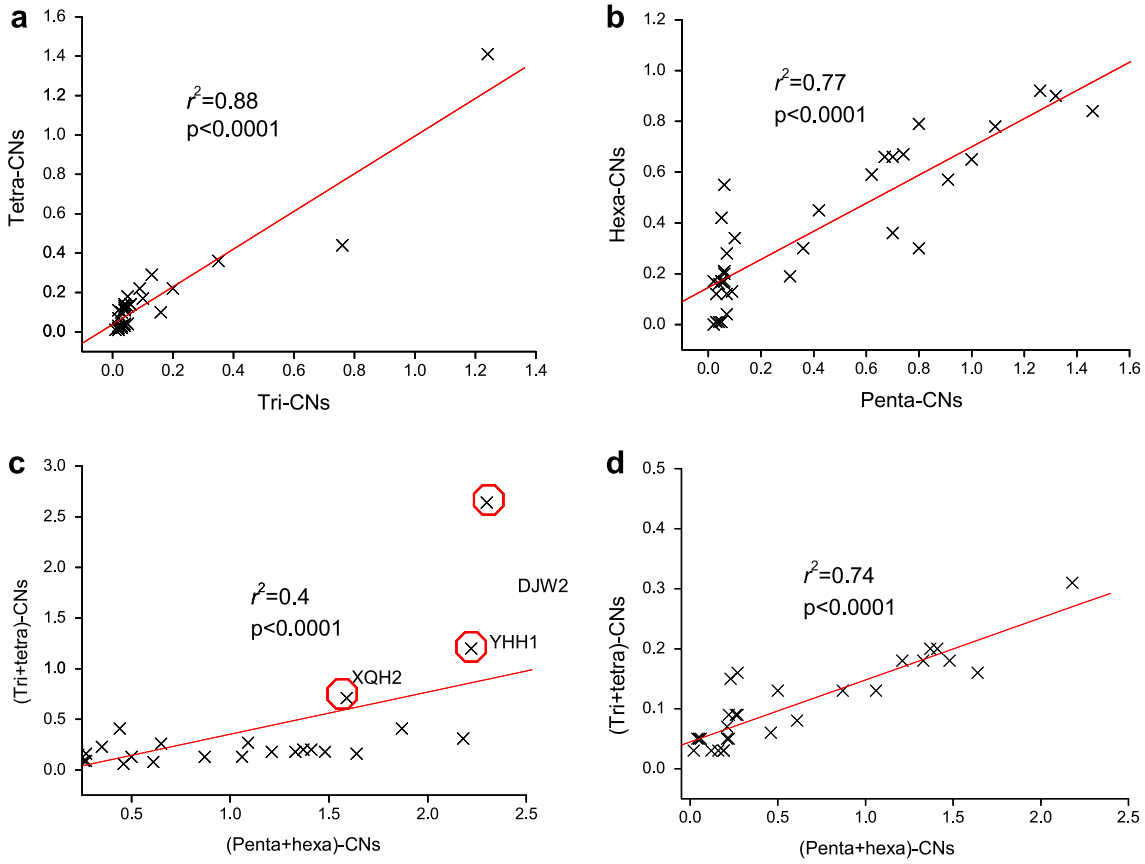

Fig. 4. Correlations between PCN homologues.

Halowax 1014 and sample surroundings, it can be indicated that PCNs in riverine sediments of the Laizhou Bay area were mainly from release of industrial usage. At certain industrial sites, there are also additional contributions from industrial thermal process.

It might be difficult to explain the industrial usage of PCNs in the Laizhou Bay area, due to the lack of information about PCN production in China. Extremely high PCN concentrations (up to 23 400 ng g^{-1} dw) were found in sediments near a former Superfund Site in America, which was surrounded by mainly chemical industries for over 75 years along the coast in last century (Kannan et al., 1998). In another study concerning pollutants from the industrial region of Bitterfeld, a major industrial site of chemical and metallurgical production in Germany in the 19th century, 2540 ng g^{-1} of PCNs were found in riverine sediments(Brack et al., 2003). By contrast, in the Laizhou Bay area with similar dense industries, it was 4–5 orders of magnitudes lower, despite PCN concentrations in developed countries have undergone a sharp decrease in the last 40 years due to the decline of production and industrial use (Gevao et al., 2000; Meijer et al., 2001; Yamashita et al., 2000b). Thus it was unlikely that technical PCN formulations were widely used in industries in the Laizhou Bay area. PCB usage was also proved to be a big contributor of PCNs in some regions. In present study however, poor correlation was observed between the concentrations of ∑PCNs and ∑PCBs (unpublished data). ∑PCNs/∑PCBs values were >0.2 in ~80% of the sites with a mean value of 0.82. It's over ten folders higher than those found in the air of a global study and 4–5 orders of magnitude higher than those in the PCB formulations (Lee et al., 2007; Yamashita et al., 2000a). Thus, the contributions from PCB usage might be also very limited. It was reported that companies in Japan imported rubber materials contaminated with PCNs during 1998–2001, reused them and put them on the market. This could also be the case happening in China and PCNs existing as impurities in industrial materials were probably a big contributor to the wide prevalence in Laizhou Bay area.

3.4. Riverine input of PCNs from rivers to the coastal ocean

Riverine runoff is an important mode to transport anthropogenic pollutants from terrestrial sources to adjacent oceans. Lack of runoff samples from the rivers though, quite a lot of interesting information can be extrapolated when comparing the profiles of marine sites and estuarine sites, as showing in Fig. 5.

In marine sediments, penta- and/or hexa-CNs were relatively higher than other homologues in most of the samples, with a mean proportion of 36% and 42%, respectively. Specifically, the profiles varied pretty much along the west and south coast. For instance, hexa-CNs were predominant in site F1 and F3, with a proportion of more than 65%; penta- and hexa-CNs account for more than 90% in site F2; while at site E4 and E5, proportion of each homologue varied little.

Compared with estuarine sites, high resemblance was observed, as show in the direction of dotted arrow in Fig. 5. It is obvious that site F1 was mainly contributed by GLH, site F2 by DJW drainage system and XQH, site F3 by MH and BLH, while site E4 and E5 were mostly influenced by the combination of DH, WH and JLH. This is consistent with PCN concentration distributions in the bay. The coastal sites impacted by industrial area have higher PCN concentrations than those influenced by the rural. Therefore, a strong riverine input of particles was suggested and this can also explain

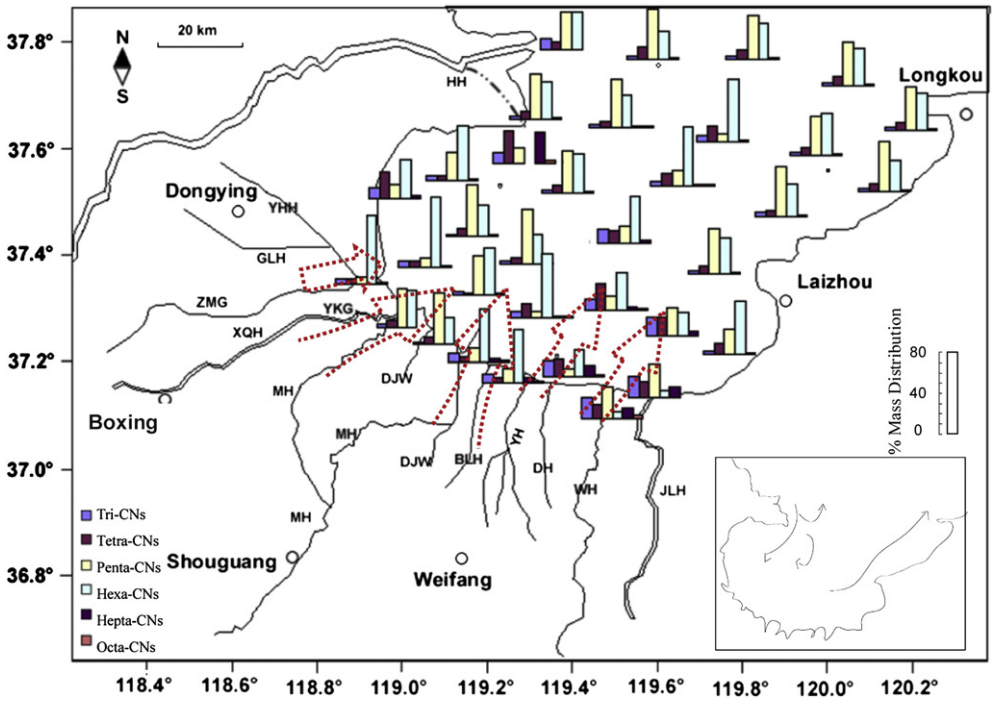

Fig. 5. Homologue mass percentage of samples collected from bay sites and river estuaries (note: in DH, WH and BLH, riverine sediments nearest from the estuary were used due to the lack of estuarine samples; graph in the lower right corner is the tidal current schematic diagram in Laizhou Bay, cited from the Compiling Committee, 1991).

the variability in profiles along the coast. Besides, despite of the shallow sea water and frequent storm tide which may result strong hydrodynamic turbulence along the coast, it can be indicated from our results that there is very little impact on PCN distributions in the coastal area. On the east coast, relatively high concentrations were also found and their compositional profiles were similar with those in most chemical industrial river sites. This is probably attributed to two cities – Laizhou and Longkou, which located on the east coast. They have similar industries with Binhai Zone. Therefore, it can be suggested that PCNs along the coast of Laizhou Bay were mainly controlled by riverine input of particles. While into the central bay, no gradient concentration in seaward trend was observed and their profiles were dominant by penta- and/or hexa-CNs. This is probably attributed to several reasons. Unlike coastal area which was directly influenced by near river sources, marine particles in central bay are mixed from different riverine input. Besides, they are surely moved under hydrodynamic force. Thus during the mixing and moving process, concentration distributions and the equilibrium partitioning between surrounding water phase and sediments might have changed. This could possibly be further proved by their reduced correlation coefficients among PCN homologues in marine environment.

4. Conclusion

This work provided much information on the pollution status of PCNs in riverine and marine sediments in the Laizhou Bay area. PCNs in the Bay were at the lowest end of the range found world wide, and the levels of PCNs in rivers were similar with many studies in Europe, including the backgrounds, bays and marine coast. PCN concentrations in riverine sediments varied according to their sampling surroundings and a strong influence of direct discharge from local factories was suggested. Compositional profiles between samples and Halowax 1014 were compared and correlations between PCN homologues were made, and it was indicated that PCNs in riverine sediments of the Laizhou Bay area were mainly from release of industrial usage with additional contributions from industrial thermal process at some sites. Profiles of coastal sediments were consistent with those of estuarine sites and thus it was suggested that PCNs along the coast of Laizhou Bay were mainly controlled by riverine input of particles. While in the central bay, PCN distributions were possibly impacted by combined multiple factors.

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